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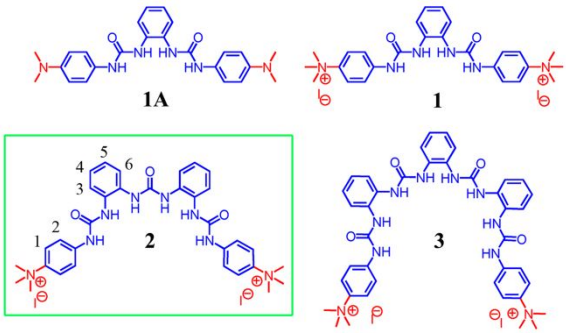
Recognition of (thio)sulfate and phosphate in aqueous solutions has been demonstrated by using oligo-urea-based receptors functionalized with quaternary ammonium groups. The ammonium groups allow for increased aqueous solubility while simultaneously providing positive Coulombic interactions and stronger hydrogen bonding through an inductive effect. This simple and generally applicable modification provides an effective way to bolster the anion binding and water solubility of oligo-urea-based receptors. With a water soluble receptor 2, selective binding of adenosine phosphates was achieved at physiological pH.

(Thio)sulfate and phosphate, are anions of vital importance in biological systems. Sulfate (SO_4^{2-}) is the fourth most abundant anion in human plasma (0.27 mM), and is the major sulfur source for biosynthesis of sulfated compounds, including mucopolysaccharides, glycoproteins, lipids, and steroids;[1] Thiosulfate ($S_2O_3^{2-}$) is believed to have natural regulatory functions, and deficiency in sulfur metabolism can be related to cancer, virus infection and immunodeficiency;[2] Phosphate ions ($H_2PO_4^-$, HPO_4^{2-}), together with heterocyclic bases and sugars, make up adenosine phosphate, DNA and various phosphorylated proteins to accomplish such vital functions as energy storage and signal transduction.[3] In this context, it's of significance to develop artificial receptors for sensing, extraction or transmembrane transport of (thio)sulfate and phosphate.[4] However, only very a few receptors can work in water and applications in biological environments are limited.[5] Because of the extremely hydrophilic nature of (thio)sulfate and phosphate, recognition of these anions in water remains a challenge, which necessitates the use of receptor with complicated and elaborate structures to overcome the strong competition of water.[6] A consequence of this increased complexity is often decreased water solubility of the receptor.



Scheme 1. Design strategy of water-soluble sulfate receptors, showing **1A** as a model receptor and **1-3** as quaternary ammonium functionalized oligo-ureas with increasing binding sites (water soluble receptor **2** was highlighted with a frame).

To this end, strongly binding yet water soluble anion receptors have been developed base on charged groups, such as oligo-ammoniums[7] and oligo-guanidiniums.[8] However, the oligo-ammonium-based receptors usually present poor selectivity in large part due to the lack of directionality in their Coulombic interactions.[5c] Though selective, the oligo-guanidine-based ones are difficult to synthesize.

Recently, *ortho*-phenylene bridged oligo-ureas, such as bis-, tris- and tetra-ureas (Scheme 1), have been proved as selective receptors for sulfate/phosphate.[9] While these oligo-ureas present low to non-existent solubility in aqueous environments, rendering them unusable for selective complexation of aqueous anions. We are interested in developing a new generalized strategy for the development of water-soluble sulfate/phosphate receptors by combining the advantages of both ionized- and oligo-urea-based systems. It was hypothesized that the addition of quaternary ammonium groups to oligo-urea-based receptors would lead to a water-

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soluble and reinforced binding system. A positive charge built into the oligo-urea will not only increase water solubility and give an advantageous Coulombic interaction, but will also increase the acidity of the urea N-H bonds leading to an increase in binding strength.[10] Moreover, the importance of Coulombic interaction has been demonstrated in the selective crystallization of dicopper(I) by using naphthalene-1,5-disulfonate as the counter anion.[11]

To explore the utility of this approach for making effective (thio)sulfate and phosphate receptors, a series of these receptors were designed based on a oligo-urea core with the addition of an N,N,N-trimethylanilinium group as the charged component (Scheme 1). Synthesis of the desired receptors proceeded from previously synthesized dianiline precursors.[9d-f] Refluxing these compounds in THF in the presence of 4-isocyanato-N,N-dimethyl aniline yielded the corresponding neutral receptors and subsequent methylation afforded the iodide-salt of the doubly charged derivatives (**1**-**3**).[12] With the three receptors in hand, the solubility of the sulfate complexes were compared with that of neutral receptor **1A** (Table 1).

Table 1 Solubility limits (v/v, water) of the sulfate complexes of receptors **1**-**3** at 298K in aqueous DMSO-d_6 and the corresponding sulfate-binding constants (K_a, M^{-1})[a].

Complexes	Solubility limits (v/v, water)	K_a (DMSO/ 20% H_2O)	K_a (DMSO/ 50% H_2O)	K_a (100% D_2O)
1A•SO_4^{2-}	20%	2791	_[b]	_[b]
1•SO_4^{2-}	95%	>10^4	1145	_[b]
2•SO_4^{2-}	100%	_[b]	3425	390
3•SO_4^{2-}	80%	_[b]	9012	_[b]

[a] All errors < 10% except where noted; [b] Not determined;

For each receptor, a 1.25 mM solution was prepared in DMSO mixed with different amounts of water, and tetrabutylammonium (TBA) sulfate was added in a stoichiometric amount. The solutions were observed for turbidity, and the upper limit of water tolerance was recorded. The neutral receptor, **1A**, precipitated when the percentage of water (v/v) reached more than 20%. As expected, the charged analogue **1**, showed a drastically increased solubility remaining in solution until a threshold of 95% water was reached. The other charged receptors, **2** and **3,** demonstrated solubility in up to 100% and 80% water respectively. In this regard, **2** achieved our initial goal of solubility in pure water while the other receptors were soluble in aqueous solutions. All three complexes showed increased solubility in comparison to the control receptor, **1A**.

Sulfate binding constants of the four receptors were determined by ^{1}H NMR spectroscopy in aqueous solutions. To minimize the ion-pairing effect, $(TBA)_2SO_4$ was utilized to titrate with each receptor and binding constants were calculated by fitting titration profiles of NH or CH to a 1:1 binding model with the WinEQNMR2 software (Table 1, see ESI, Fig. S19-S27).[13] The efficacy of adding the charge on the receptors is clearly seen when comparing the binding constants of **1** and **1A** in DMSO-d_6/20% H_2O. The neutral receptor, **1A**, demonstrates a K_a of 2791 M^{-1} while **1** has a binding constant that is > 10^4 M^{-1} (the upper limit that can be determined accurately by NMR),[13] over an order of magnitude greater. It is thus apparent that simply adding a complementary charge to a receptor has the capability of greatly increasing its affinity for sulfate. This effect was attributed to the Coulombic interaction, and enhanced acidity of the adjacent urea groups which was evidenced by the relative downfield shifts of the urea protons of **2** compared with the un-methylated precursor **2A** (Fig. S28). The other charged receptors also competently bind sulfate in aqueous solution, and show the expected trend of increasing affinity for sulfate as the number of hydrogen bond donors increases (from **1** to **3)**. Of considerable note is the ability of **2** to bind sulfate in pure D_2O. Upon adding increasing amounts of SO_4^{2-} to the solution of **2**, the protons of **2** in the terminal phenyl (CH1 and CH2) and NMe_3 showed continuous upfield shifts, which allowed determination of the binding constant as 390 M^{-1} by fitting the titration profile of CH1 (Fig. S24). This success was attributed to the synergetic effect of hydrogen bonding and Coulombic interactions, because when using a control dication molecule, 1,3-bis(trimethylammonium)benzene,[14] no significant binding was observed with sulfate in D_2O (Fig. S29).

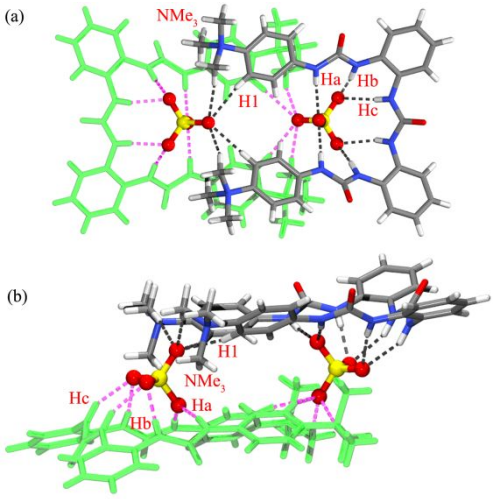

Fig. 1 Crystal structures of complex $[(\mathbf{2})_2^{2+}\cdot(SO_4)_2^{2-}]$, shown as a dimer in (a) a top-down view and (b) side view (hydrogen bonds are shown as dashed lines; solvent molecules are omitted for clarity).

More details of the sulfate binding was obtained from the single crystal structure, $[(\mathbf{2})_2^{2+}\cdot(SO_4)_2^{2-}]$, which showed a 2:2 dimer assembly (Fig. 1). The receptor maintained a planar orientation with little distortion, and all of the urea protons were coordinated with the sulfate. Three out of four oxygen atoms of SO_4^{2-} were bound by six hydrogen bonds with N···O distances ranging from 2.8094 to 2.8990 Å (2.8730 Å on average) and N-H···O angles from 147° to 175° (163° on average). The fourth sulfate oxygen was bound by four CH protons from the other receptor, with the anilinium methyl groups and phenyl groups donating two hydrogen bonds each,

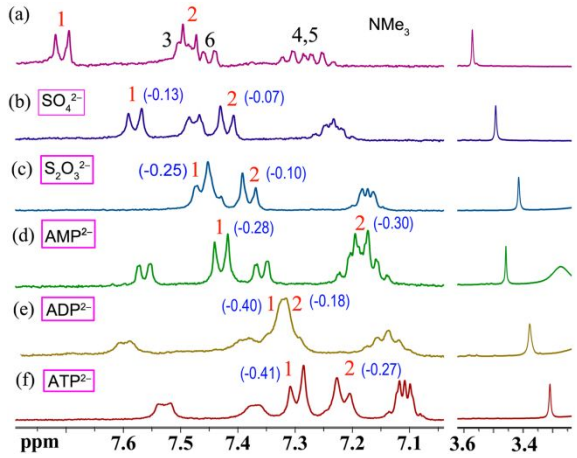

Fig. 2 Partial ^{1}H NMR spectra (400 MHz, 298 K, pH 7.4 D_2O buffered by 20 mM HEPES) of (a) free receptor **2** (1.25 mM) and (b) **2**/25 SO_4^{2-}, (c) **2**/25 $S_2O_3^{2-}$, (d) **2**/25 AMP^{2-}, (e) **2**/0.5 ADP^{2-} and (f) **2**/0.5 ATP^{2-} (all anions added as sodium salts, numbers in brackets are the shifts/ppm of CH1 and CH2).

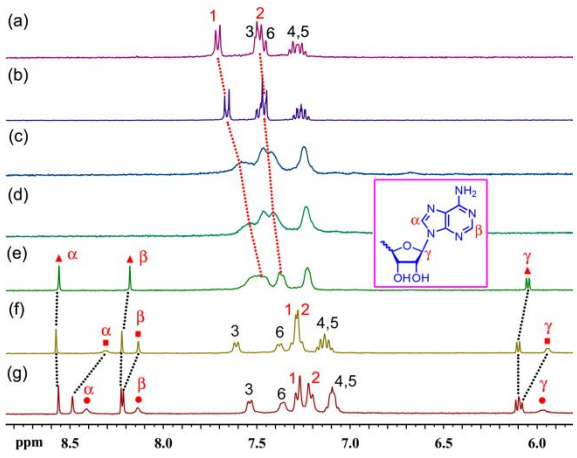

Fig. 3 Partial ^{1}H NMR spectra (400 MHz, 298 K, pH 7.4 D_2O buffered by 20 mM HEPES) of (a) free receptor **2** (1.25 mM) and after successive addition of (b) 1.0 equiv. of SO_4^{2-}, (c) 1.0 equiv. of HPO_4^{2-}, (d) 1.0 equiv. of $S_2O_3^{2-}$, (e) 1.0 equiv. of AMP^{2-} (▲), (f) 0.5 equiv. of ADP^{2-} (■) and (g) 0.5 equiv. of ATP^{2-} (●, all anions added as sodium salts, inset: proton numbering of the adenosine group).

wherein the C···O distances ranged from 3.3234 to 3.4035 Å (3.3583 Å on average) and C-H···O angles from 161° to 172° (166° on average, see ESI for more details).

To investigate the possible formation of such a dimer in solution, DOSY of receptor **2** and **2**/5 $(TBA)_2SO_4$ were performed in DMSO-d_6 solutions (Fig. S30,S31). Accordingly, the radius of **2**/5 $(TBA)_2SO_4$ is 1.3 times larger than **2**, which is consistent with a 1:1 binding mode, because otherwise the radius of **2**/5 $(TBA)_2SO_4$ would be about 2 times larger than **2** if in a 2:2 binding mode.

With the water soluble receptor **2**, the selectivity for various anions (all added as sodium salts) was studied by ^{1}H NMR in buffered D_2O at physiological pH (7.4, 20 mM HEPES). All tested monoanions (Cl^-, NO_3^-, HCO_3^-, ClO_4^-, AcO^- and $H_2PO_4^-$) showed no detectable binding with **2** neither in buffered D_2O nor in pure D_2O (Fig. S32, S33). In contrast, dianions (SO_4^{2-}, $S_2O_3^{2-}$, AMP^{2-} = adenosine monophosphate, ADP^{2-} = adenosine diphosphate and ATP^{2-} = adenosine triphosphate), induced dramatic upfiled shifts of signals of **2** (CH1, CH2 and NMe_3, Fig. 2; see Scheme 1 for the numbering of protons), and the titration profiles were well fitted to a 1:1 (for SO_4^{2-}, $S_2O_3^{2-}$, AMP^{2-}) or a 2:1 (host:guest) binding model (for ADP^{2-} and ADP^{2-}), giving binding constants as $K(SO_4^{2-})$ = 235 M^{-1}, $K(S_2O_3^{2-})$ = 295 M^{-1}, $K(AMP^{2-})$ = 549 M^{-1}, $K(ADP^{2-})$ > 10^4 M^{-2} and $K(ATP^{2-})$ > 10^4 M^{-2} (Fig. S34-S40). Although HPO_4^{2-} also induced dramatic spectra changes, the binding constant was not determined due to coexistence of multiple equilibriums as suggested by job plot and severely broadened spectra (Fig. S39, S40).[15] Alternatively, it was estimated as comparable with $K(SO_4^{2-})$ and $K(S_2O_3^{2-})$ based on the fact that the sharp spectrum of **2**/1.0 SO_4^{2-} turned broad and signals of CH1 and CH2 showed continuous upfield shifts after addition of equal amount of HPO_4^{2-} followed by $S_2O_3^{2-}$ (Fig. 3b-d). Given the similar geometry (tetrahedron) and electron density, it's not surprising that SO_4^{2-}, HPO_4^{2-} and $S_2O_3^{2-}$ presented similar binding affinity, and the small differences may come from distinctions in hydration energy.[6, 16]

It's notable that AMP^{2-} presented stronger binding with **2** than the inorganic anions. In the presence of equal one equiv. of inorganic anions (SO_4^{2-}, HPO_4^{2-} and $S_2O_3^{2-}$), AMP^{2-} induced a spectrum similar with that induced by AMP^{2-} alone, which indicated that receptor **2** prefers to bind AMP^{2-} over the inorganic anions (Fig. 3e, Fig. S41). This was attributed to additional contributions from π•••π interactions between AMP^{2-} and **2**, as indicated by the upfiled shifts of signals of both the adenosine group of the former (Fig. S41, $\Delta\delta$ = -0.05 to -0.06 ppm) and the terminal phenyl rings of the latter (Fig. 2e, CH1, $\Delta\delta$ = -0.28ppm and CH2, $\Delta\delta$ = -0.30 ppm).

After further addition of 0.5 equiv. of ADP^{2-} to the solution, the spectrum became similar with that induced by ADP^{2-} alone and the signals of AMP^{2-} showed as a free state, suggesting the AMP^{2-} was replaced by ADP^{2-} in the binding with **2**. In a similar manner, the subsequently added 0.5 equiv. of ATP^{2-} replaced the ADP^{2-} (Fig. 3f.g). The stronger binding with ADP^{2-} and ATP^{2-} than with AMP^{2-} was rationalized by the 2:1 (host:guest) binding mode, which induced stronger π•••π interactions between their adenosine groups and the terminal phenyl rings of **2**. This was evidenced by the more significant upfield shifts of their adenosine groups (Fig. S42, $\Delta\delta$ = -0.06 to -0.17 ppm for ADP^{2-}; $\Delta\delta$ = -0.27 to -0.30 ppm for ATP^{2-}) than in the case of AMP^{2-}.

So, anion competition experiments showed the anion selectivity of receptor **2** follows an order as ATP^{2-} > ADP^{2-} > AMP^{2-} > $S_2O_3^{2-}$, HPO_4^{2-}, SO_4^{2-}. When increasing the concentrations of inorganic anions (SO_4^{2-}, HPO_4^{2-} and $S_2O_3^{2-}$), AMP^{2-} failed to compete with 5 equiv. of the former, while ATP^{2-} and ADP^{2-} could keep well prior binding in the presence of 10 equiv. of the inorganic anions (Fig. S43).

In conclusion, we have demonstrated an effective strategy to increase water solubility and enhance anion binding affinity of oligo-urea-based receptors by simply functionalizing the terminal with two ammonium groups. With a water soluble receptor **2**, selective binding of adenosine phosphates (ATP^{2-}, ADP^{2-}, AMP^{2-}) over inorganic dianions ($S_2O_3^{2-}$, HPO_4^{2-} and

SO_4^{2-}) was achieved at physiological pH, which was attributed to synergetic binding of both the phosphate and the adenosine groups through hydrogen bonding and π•••π interactions, respectively. Given the importance of (thio)sulfate/phosphate binding in water, this study will provide a significant foothold for those wishing to explore future applications of these receptors in biological systems, such as transmembrane transport and selective sensing of adenosine phosphates.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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